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COMMUNICATION

A mesoporous metal-organic framework constructed from a nanosized C_3 -symmetric linker and $[Cu_{24}(isophthalate)_{24}]$ cuboctahedra^{†‡}

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The mesoporous framework $[Cu_3(L)(H_2O)_3] \cdot (DMF)_{35} \cdot (H_2O)_{35}$ (NOTT-119) shows on desolvation a BET surface area of 4118(200) m² g⁻¹, a pore volume of 2.35 cm³ g⁻¹, a total H₂ uptake of 101 mg g⁻¹ at 60 bar, 77 K and a total CH₄ uptake of 327 mg g⁻¹ at 80 bar, 298 K.

Porous metal-organic frameworks (MOFs) are an important class of crystalline materials with intriguing structural topologies and tuneable pore properties. Those containing well-defined mesopores (i.e., pore diameters in the range 2-50 nm) have attracted increasing attention due to their potential applications in energy/gas storage,^{1,2} CO₂ capture,³ catalysis,⁴ sensing⁵ and drug delivery.⁶ However, the search for structures with very large pores (*i.e.*, with diameters up to 3 nm) still presents great challenges. The use of longer organic linkers to construct MOFs incorporating giant pores/cavities is a promising strategy, but one which also tends to lead to interpenetrated structures,^{7,8} and this drastically reduces the available surface area and pore size. Moreover, linker expansion tends to dramatically reduce the stability of the framework, leading to its partial or total collapse upon removal of solvents from the porous host.^{8a,9} We report herein an extended nanosized hexacarboxylate linker which has enabled the synthesis of a stable mesoporous (3,24)-connected framework⁹⁻¹² with Cu(II) (denoted as NOTT-119) incorporating cages of up to 4.3 nm in length. NOTT-119 is isostructural with the frameworks NOTT-112,¹⁰ NOTT-116,¹¹ PCN-61,⁹ PCN-610⁹ and NU-100.^{12d,e}

The new extended linker H_6L (Scheme 1) was synthesised via Pd(0)-catalyzed Suzuki coupling of the extended tri-iodo precursor 1,3,5-tris(4'-iodobiphenyl)benzene and 3,5-di(ethoxy-carbonyl)phenylboronic acid in good yield (see ESI†). Solvothermal reaction of H_6L with Cu(NO₃)₂·3H₂O in

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^c Diamond Light Source, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK *N*,*N*-dimethylformamide (DMF) in the presence of a small amount of HCl at 90 °C afforded blue crystals of $[Cu_3(L)(H_2O)_3]$ ·(DMF)₃₅·(H₂O)₃₅ (NOTT-119).

The single crystal X-ray structure of NOTT-119 confirms the formation of a **ubt**-type¹³ network incorporating cuboctahedral cages constructed from 12 $\{Cu_2(O_2CR)_4\}$ paddlewheels and 24 isophthalates from 24 different L^{6-} linkers (Fig. 1). The structure comprises fused cuboctahedral (Cage A), truncated tetrahedral (Cage B) and truncated octahedral (Cage C) cages. Significantly, despite the exceptionally long organic linker, the structure of NOTT-119 is non-interpenetrating and the (3,24)connected structure affords a system in which the distance between the carboxylates in adjacent arms of L⁶⁻ defines the spacing between adjacent cuboctahedra (Cage A; inner sphere diameter ca. 13 Å). This generates the mesocavities of Cage B and C, which have, taking into account van der Waals radii, inner sphere diameters of ca. 2.41 and 2.5 nm, respectively, the longest cage length being ca. 4.3 nm for Cage C. The total solvent-accessible volume of the desolvated framework was estimated¹⁴ to be 84.2% (after removal of guest solvates and coordinated water molecules) making it one of the most porous MOF materials synthesised to date.^{12d,15-17} The largest aperture in NOTT-119 is estimated to be 1.9 nm in diameter, and the bulk crystal density for desolvated NOTT-119a was calculated to be 0.361 g cm⁻³.

TGA of solvated NOTT-119 under N_2 showed loss of solvent (DMF and water) below 135 °C, with the framework stable up to 315 °C, beyond which the material decomposes (see ESI†). The solvent molecules in the as-synthesised solids were exchanged with acetone several times to ensure that



Scheme 1 View of L^{6-} , the organic linker in NOTT-119, and $(L^{1})^{6-}$, the organic linker in NOTT-116.

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Fig. 1 View of the three types of cages in NOTT-119. Spheres indicate the void space within the three types of cavities (Cage A, violet; Cage B, turquoise; Cage C, yellow). Hydrogen atoms and disordered solvent molecules are omitted for clarity. Carbon, black; oxygen, red; copper, turquoise.

DMF was completely replaced by low-boiling point acetone, and the desolvated framework NOTT-119a was generated by heating the acetone-exchanged sample at 110 °C for 16 h under dynamic vacuum. Significantly, the crystal lattice of this activated sample remains intact on extended heating under vacuum, as confirmed by powder diffraction analysis (see ESI[†]). Thus, crystallinity and order of the (3,24)-connected polyhedral framework architecture is retained in NOTT-119a. However, when the size of the linker is extended beyond this point, the network is no longer stable to thermal treatment and suffers disruption of the structure due to surface tension effects. Thus, the isostructural Cu(II)-based (3,24)-connected material NU-100^{12d} (also known as PCN-610⁹), which incorporates a slightly longer linker than that in NOTT-119, undergoes complete loss of crystallinity on thermal desolvation under vacuum. However, this mesoporous network retains crystallinity on desolvation using supercritical CO₂.^{12d}

The N₂ isotherm for NOTT-119a shows (Fig. 2) typical Type IV behaviour with a slight adsorption-desorption hysteresis in the P/P_0 range 0.05–0.25, indicative of the presence of mesopores. The pore-filling step in NOTT-119a is shifted to a higher pressure $(P/P_0 = 0.25)$ compared to a value for $P/P_0 =$ 0.15 for NOTT-116a,¹¹ which incorporates an alkyne moiety in place of one of the phenyl groups in each arm of the ligand $(L^{1})^{6-}$ (Scheme 1). This indicates that the accessible cages in NOTT-119a have larger pore diameters. NOTT-119a exhibits exceptionally high N₂ uptake of *ca*. 1522 cm³ g⁻¹ at saturation and a remarkably high total pore volume of 2.35 cm³ g⁻¹, among the highest reported for MOF materials. By applying the Brunauer-Emmett-Teller (BET) model in the pressure range $P/P_0 = 0.12$ to 0.18, the specific surface area of NOTT-119a was calculated to be 4118(200) $m^2 g^{-1}$ (see ESI[†]), making it one of the few MOFs with a BET surface area exceeding 3800 m² g⁻¹.¹⁸



Fig. 2 N_2 and Ar isotherms for NOTT-119a at 77 and 87 K, respectively.

The Ar sorption isotherm for NOTT-119a reveals stepwise adsorption and desorption with a significant desorption hysteresis over the pressure range P/P_0 0.08–1.0 (Fig. 2). In the Ar adsorption branch, the first distinctive step is at $P/P_0 =$ 0.27, and there is a second step at $P/P_0 = 0.66$. The Ar desorption branch shows hysteresis due to condensation within the mesopore,¹⁹ and three steps at $P/P_0 = 0.19, 0.1, and 0.08$ reflecting the unique hierarchical assembly of polyhedral cages in this material. NOTT-119a shows an extremely high Ar uptake of *ca*. 2000 cm³ g⁻¹ at saturation, and the pore size distribution was determined by analyzing the Ar adsorption isotherm using non-local density functional theory (NLDFT) (see ESI[†]). This revealed a distribution of mesopores (2.4-3.4 nm) consistent with the crystallographically-determined diameters of Cage B and Cage C. In addition, there is a narrow distribution of mesopores (6.1-7.1 nm) corresponding to the mesoporous channels formed by the windows of the extra-large cavities in NOTT-119a. Compared to NOTT-116a,¹¹ the pore volume of NOTT-119a is higher (2.35 vs. 2.17 cm³ g⁻¹, respectively), but the surface area is lower (4118 vs. 4664 m² g⁻¹). Thus, NOTT-119a appears to be near a cusp where increasing pore volume occurs at the expense of the overall surface area of the porous host. Since gas storage capacities of porous MOFs are controlled by the isosteric heat of adsorption of the substrate at low pressures, by surface area of the host at moderate pressures, and by pore volume at high pressures (close to saturation),^{7,10,11,20} we investigated the high pressure uptake of both H₂ and CH₄ by NOTT-119a.

High pressure H₂ sorption isotherms for NOTT-119a up to 60 bar at 77 K were collected using a volumetric measurement method, and this confirmed (Fig. 3) an excess H₂ uptake of 59 mg g⁻¹, equivalent to 5.6 wt% [wt% = 100(weight of adsorbed H_2 /(weight of host material + weight of adsorbed H₂)] at 44 bar. This value, although high, is lower than those of the structural analogues NOTT-112a (76 mg g^{-1} at 35 bar; BET surface area 3800 m² g⁻¹, pore volume 1.62 cm³ g⁻¹)¹⁰ and NOTT-116a (68 mg g^{-1} at 27 bar).¹¹ Given the large pore volume of NOTT-119a we anticipated that it would be in the high pressure region that this material would be most effective. This is indeed the case and NOTT-119a shows a high total H₂ uptake of 101 mg g^{-1} , equivalent to 9.2 wt% at 77 K and 60 bar, which is among the highest total H₂ uptake capacities so far observed for a MOF material.^{9–11,12d,16} NOTT-119a shows a total volumetric H₂ uptake of 37 g L^{-1} at 77 K and 60 bar (see ESI[†]) reflecting its low density. The isosteric heat of H₂ adsorption at zero coverage is 7.3 kJ mol⁻¹ (ESI⁺) consistent with the presence of exposed Cu(II) sites within the microporous $[Cu_{24}(isophthalate)_{24}]$ cuboctahedral cages.¹¹



Fig. 3 H_2 (left) and CH₄ (right) sorption isotherms for NOTT-119a at 77 K and 298 K, respectively.

CH₄ uptake by NOTT-119a was measured at 298 K and at pressures of up to 80 bar using the same sorption apparatus as used for the H₂ uptake experiments. While NOTT-119a shows a respectable excess CH_4 uptake of 154 mg g⁻¹ at 35 bar (Fig. 3), this is lower than 186.1 mg g^{-1} reported for the isostructural PCN-689 (also known as NOTT-116) under the same conditions. Due to its low crystallographic density, NOTT-119a has an excess volumetric CH₄ uptake (v/v) of 77.7 cm³ (STP) cm⁻³ at 35 bar. The excess adsorption reaches saturation with an uptake of 194 mg g^{-1} (97.8 cm³ cm⁻³) at 66 bar, and the total uptake was calculated to be 327 mg g^{-1} (165 cm³ cm⁻³) at 80 bar. These values for gravimetric CH_4 uptake in the high pressure region are comparable to other high methane-storage MOFs such as MIL-101^{2b} (excess 239 mg g⁻¹ at 80 bar), DUT-9-SCD¹⁷ (excess 219 mg g⁻¹ at 100 bar) and DUT-6^{1c}/MOF-205¹⁶ (excess 230 mg g⁻¹ at 100 bar; total 394 mg g^{-1} at 80 bar).

In summary, the (3,24)-connected mesoporous framework NOTT-119 has been synthesised by utilising a nanosized C_3 -symmetric hexacarboxylate linker. NOTT-119 shows high thermal stability due to the **ubt**-type network architecture, exhibits a high BET surface area of 4118(200) m² g⁻¹ and a remarkably large total pore volume of 2.35 cm³ g⁻¹. Desolvated NOTT-119a shows interesting Ar sorption behaviour with large desorption hysteresis, consistent with the unique polyhedral structure incorporating different sized cages, in addition to high H₂ and CH₄ adsorption capacities in the high pressure region.

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